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Hollow Fiber Membranes in Increased Algae Growth for Biobutanol Production

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Hollow Fiber Membranes in Increased Algae Growth for Biobutanol Production

An Undergraduate Honors College Thesis

in the

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College of Engineering
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by

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ABSTRACT

Algae are a unique and remarkable species of plant that is capable of thriving on land deemed useless for the cultivation of food crops. They also breathe in the harmful greenhouse gas, carbon dioxide. As the fastest living organism to complete a life cycle, algae is the single most effective user of carbon dioxide in the world thus making it an important ally for diminishing the threat of global warming. Furthermore, algae are comprised of high concentrations of lipids, rendering it an appealing option for use in biodiesel production, specifically butanol. Increasing the algae's supply of carbon dioxide gas causes increased growth, multiplying the amount of algae, and, therefore, the amount of lipids harvested making algae oil a viable option for the next biodiesel feedstock. Research reveals that algae grow at a quicker pace near carbon dioxide emitting power plants; however, experiments have proven successful that utilized the use carbon dioxide permeable hollow fiber membranes to deliver a high concentration of pure carbon dioxide gas to algae in a laboratory setting. The hollow fiber membranes used previously have been shown to demonstrate a low tolerance to physical strain caused by harvesting the algae. The hollow fiber spinning apparatus I have designed will allow modification of the current membrane design for optimum results in the outdoor biological system, thus increasing the amount of algae further, thus increasing the amount of biofuel produced by a system.

INTRODUCTION

The race for an economical and efficient alternative fuel source is well underway in the United States and around the world. Biomasses for these alternative fuels have been proposed across the spectrum of terrestrial plants from corn and switch grass to sugar cane and canola. However, algae is a lucrative potential candidate for biofuel biomass due to its rapid lifecycle, its non-competition with food crops, and its high lipid concentration.[1,2] Furthermore, algae species can grow in waters that are contaminated, saline, arctic, or salty, making them capable of prolific growth almost anywhere in the world.[1] Algal oil is non-toxic and can utilize the oil infrastructure already in place for fossil fuels meaning that piping systems, fuel stations, and car engines would not have to undergo significant redesign for incorporating algal oil.[3,4]

Research indicates that algae's growth rate increases when in the presence of excess carbon dioxide.[1,7] Increasing the algae's growth rate increases the amount of oil that can be produced in the same time frame by the same unit area of land, driving the cost of the oil to a more economically competitive level. Algae growing in open air ponds and in other open air environments are the most promising ways at present to mass produce enough algae to quantitatively manufacture a significant amount of biofuel.[2] Ponds in which carbon dioxide has been introduced into the water have been proven to yield larger amount of algal biomass than ponds of similar construction without additional carbon dioxide in the system.

Many unique methods for carbon dioxide addition exist, including, but not limited to, open tube bubbling and hollow fiber membranes (HFM). Studies suggest that HFM provide a more efficient way of delivering carbon dioxide gas to aquatic systems than simple open tube bubbling as shown in Figure 1.[2] Introduction of carbon dioxide via HFM has another advantage over open tube bubbling in that the HFM method uses substantially less carbon dioxide feed gas to achieve the same carbonation results as open tube bubbling.[2] The cause of the improved growth rate of the algae with HFM carbonation is the enhanced mass transfer between the carbon dioxide and the algae facilitated by the HFM. The carbon dioxide bubbles produced by HFM are significantly smaller in size than the bubbles formed by conventional bubbling. The membrane's bubbles are so small that they do not rise to the surface immediately or at all, but instead adhere to the surfaces they contact.

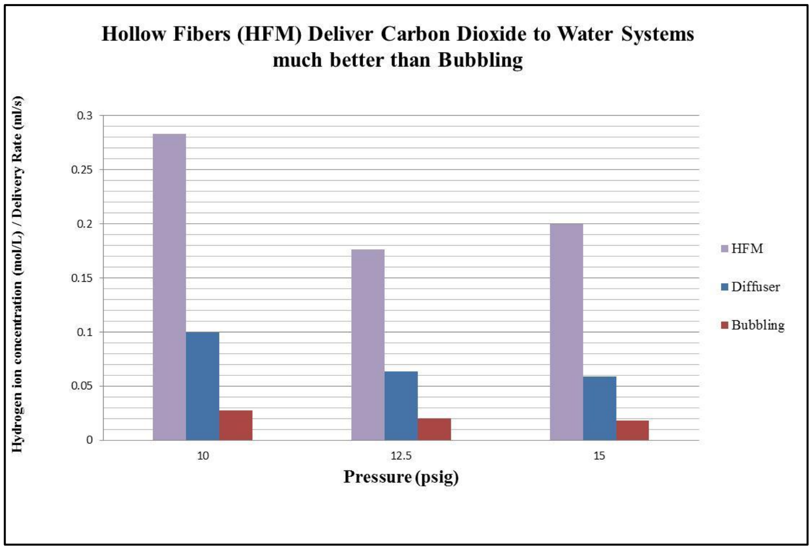

Figure 1 Results of HFM vs bubbling

Algae have been the subject of energy researchers for nearly four decades, dating back to the oil crisis of the 1970's when the United States Congress funded the National Renewable Energy Laboratory (NREL) under the Department of Energy to investigate possible alternative fuel options. Under the Aquatic Species Program (ASP), algae species high in lipid concentration grown near coal driven power plants were investigated for possible use in producing biodiesel and for their effect of reducing harmful carbon emissions from these power plants. The ASP concluded through its experiments that 15,000 gallons of oil per acre of algae could be produced per year under optimal growing conditions which is substantially more promising than prospective yields from other feedstocks found by the committee[5,4].

As was previously mentioned, by growing algae near carbon emitting power plants, the ASP was able to improve the algae's growth rate. To facilitate this need for an increase in the amount of carbon dioxide gas reaching the algae, I proposed to use carbon dioxide permeable HFM. The HFM design is flexible, has high performance ratings, and has minimum waste products therefore decreasing the cost of operation and the hazards involving waste products[6].

PROJECT OVERVIEW

The results depicted above show that HFM are capable of carbonating an algal growth system more effectively than direct open-tube bubbling; therefore, I focused my research on carbonation on HFM that are carbon dioxide permeable. In past experiments, the HFM were enclosed in their cartridge, which is the conventional method of operating HFM in practice. However, this operation in the cartridge does not allow the algae-water mixture to contact the carbon dioxide gas in the light. This is unfavorable because algae intake the majority of the carbon dioxide they utilize during their light cycle, not during the dark when they are actually secreting small amounts of carbon dioxide. Therefore, any benefits seen from carbonating the system with HFM in dark cartridges is not allowed to reach its full potential due to this biological caveat in the function of algae.

This specific application of HFM is one that has never been tested before; I am not protecting the HFM from the surroundings with the typical cartridge unit. I am instead placing the HFM directly into a biological system and exposing them to the extreme physical duress of vacuum suction (used during the harvest of the algae). I first tested this method of carbonation on a small pilot growth system I designed and constructed in a laboratory at the University of Arkansas. Since this system proved too small to adequately model a large-scale algae production facility, a larger pilot plant in Virginia was tested and produced favorable improvements in algae growth due to HFM implementation. The results of this are shown in Figure 2. As these results show, HFM in an open system were much more effective at transferring carbon dioxide to a liquid media than a diffuser or direct bubbling. Thus, the premise for this research makes sense to further explore producing hollow fiber membranes for this purpose.

The next step of my research was introduced after the continued use of HFM carbonation in the Virginia system deemed the poly-ether-ether-ketone (PEEK) commercial HFM we were using too brittle for prolonged use. After a visit to the National University of Singapore where I was instructed how to design a HFM production unit and how to operate the unit, I designed a HFM spinning apparatus for our University of Arkansas laboratory. This system is to be used to spin HFM that have a higher tolerance for physical duress.

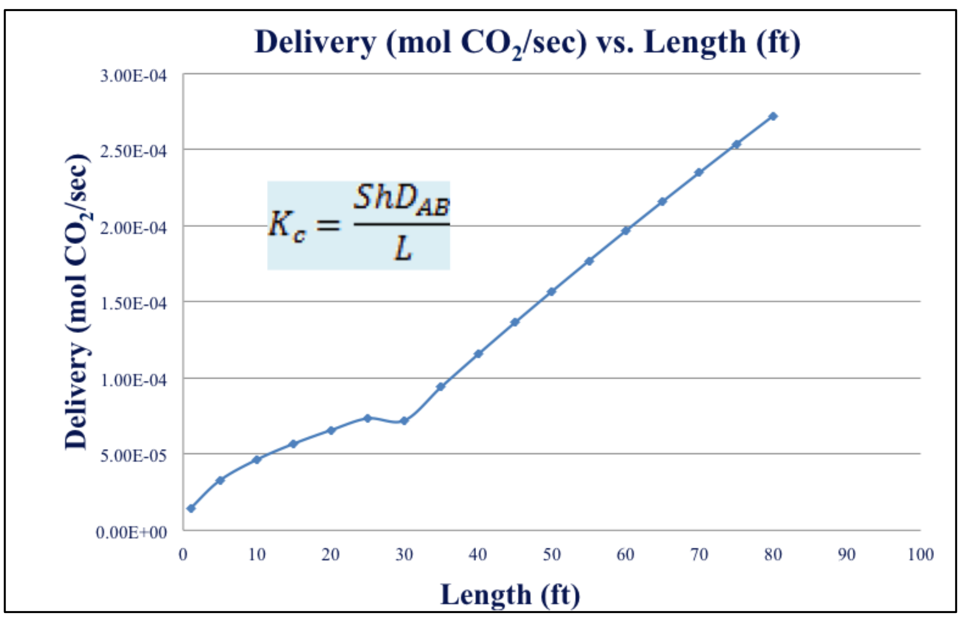

Figure 2 Modeling of carbon dioxide delivery for the length of the raceway

PILOT STUDY I—INDOOR ALGAE GROWTH SYSTEM

I designed and built a laboratory algae growth system known as a "raceway" that consisted of a stainless steel trough five and a half feet long with sides six inches tall. My algae were a strain that we gathered from a local creek and seeded onto a mesh mat that lay on the bottom of the raceway. Water from a local stream was surged down the raceway at a rate of ten gallons per minute via a pond pump and gravity draining mechanism into a large container to be recycled and surged again. The algae biomass was harvested weekly using a large industrial vacuum and was measured for dry mass. I formed a bundle of twenty commercial PEEK HFM and laid the bundle directly under the algae growth mat. The bundle was attached to a canister of pure carbon dioxide gas that was delivered directly to the algal raceway system. A picture of the system I built and designed is given in Figure 3. As shown in this Figure, this system was able to grow up algae well and many different carbon dioxide parameters were tested. This served as the model for a larger system that was later constructed by a graduate student.

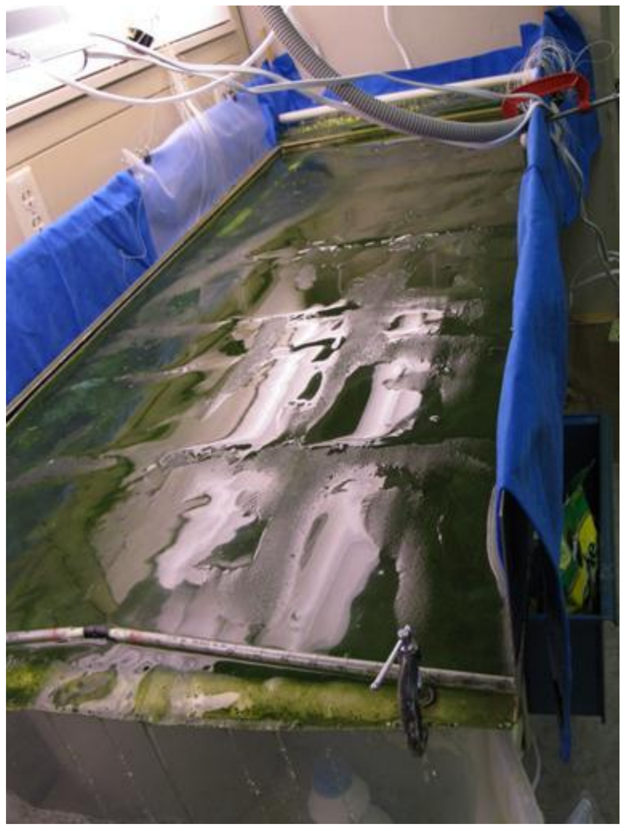

Figure 3 Picture of indoor algal raceway

PILOT STUDY II—WICOMICO VIRGINIA SYSTEM

At the conclusion of the indoor pilot study, it was evident that a larger, outdoor pilot system was required for more accurate analysis of the HFM carbonation effects. The commercial PEEK HFM were implemented under a segment of an eighty feet long by two feet wide system off the Wicomico River in Virginia. Before the HFM carbonation commenced, the algal biomass was harvested approximately every eight days with roughly constant yields by mass. After the addition of the HFM, the harvesters began harvesting the same amount of algae every three days. The delivery of carbon dioxide as a function of the length of HFM is graphically displayed in Figure 2. This shows that although the mass transfer is more significant at the beginning of the raceway, long stretches of fibers still deliver carbon dioxide over the entire length.

The algae in the Virginia system were grown on a three-dimensional mat, much like carpeting, where the bubbles were able to adhere to the entire three dimensional surface covered with algae; this adhesion caused the contact time between the algae and the carbon dioxide bubbles to be extensively longer than the contact time of large bubbles that quickly rise to the surface in conventional open-tube bubbling or the open air containing carbon dioxide gas in the case of no artificial carbonation efforts. Due to the fact that the carbon dioxide gas is not escaping into the atmosphere at a substantial rate, the amount of carbon dioxide necessary for running the system is substantially less with the fibers than straight bubbling and the carbon dioxide emissions from the system are theoretically lower as well.

One major problem with the commercial PEEK HFM used in this system was the breakage rate of the HFM. In general, HFM are manufactured without regard to physical strength because they are placed directly into cartridges that protect the HFM from any stress that would damage their structural integrity. Our HFM were breaking due to the vacuum suction that was used to harvest the algae. This breakage decreased the surface area of the fibers emitting carbon dioxide gas, and therefore decreased the rate of mass transfer of carbon dioxide to the algae, slowing the growth rate, and eventually negating the effects of the HFM altogether.

HFM SPINNING APPARATUS

Due to the problems detailed above with the commercial PEEK HFM breaking during algae harvests, I decided that I should design a method for the manufacture and design of HFM with more physical strength. This is an area of HFM development not found in the literature because it is a weakness that has never before been explored. Therefore, I travelled to the National University of Singapore to visit with Dr. Chung—a world-renowned HFM expert. There, I learned how to spin HFM and how to design an apparatus to facilitate the spinning. Upon my return to the University of Arkansas, I designed a hollow fiber membrane spinning apparatus as elucidated in Figure 4.

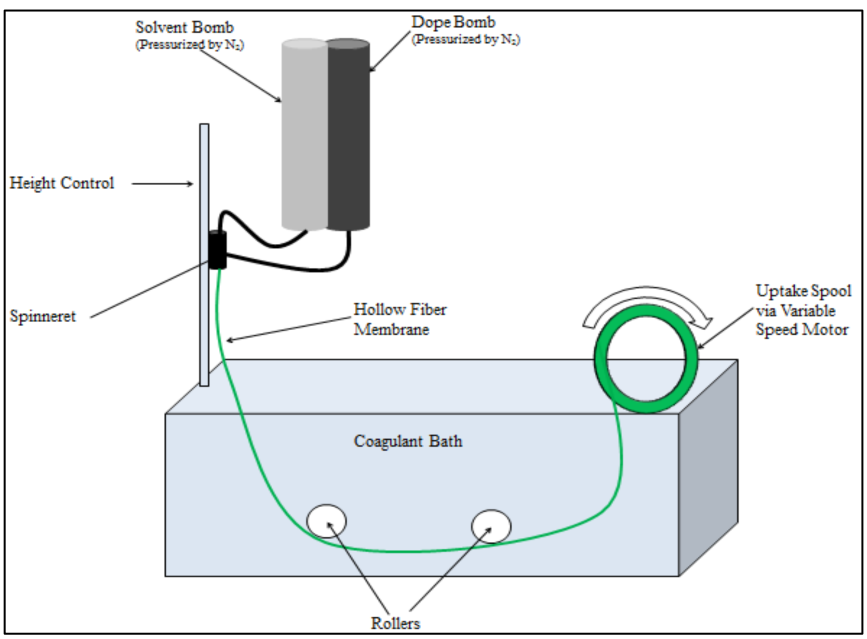

Figure 4 Diagram of HFM spinning apparatus

This apparatus can be adjusted in accordance with literature manipulations that yield certain HFM characteristics. Since mechanical strength is not reported in literature, I planned to manipulate aspects of the HFM spinning apparatus to produce HFM that are mechanically durable enough to endure the vacuum suction on a regular basis. Several parameters of the spinning apparatus can be modified to produce altered HFM such as the uptake speed, polymer and solvent flow rates, spinning height above the coagulant bath, duration of pass through coagulant bath, and many more. Any of the indicated alterations to the spinning apparatus will cause significant variances in the HFM's physical structure and properties such as thickness of the membrane's walls, porosity, and durability. The goal of this portion of my research is to optimize the design of the apparatus to produce HFM capable of withstanding the design of the algal growth system while still being permeable to carbon dioxide gas.

Unfortunately the spinning apparatus has had limitations to date. I am currently attempting to discover why the apparatus will not produce HFM when all specifications are in line with literature published experiments.

FUTURE RESEARCH AND CONCLUSION

Ideally, after optimizing my custom HFM apparatus design and performance, and producing HFM of new design, a pilot study for placement of the custom HFM in a large outdoor system for mass production of algae will be completed using the greenhouse system at the University of Arkansas. The HFM will be connected to a constant source of pure carbon dioxide gas and the algae's growth rate will be regularly recorded for analysis. According to the recorded data and analysis, the spinning apparatus can be altered further and, therefore, the HFM to improve the algal growth system design for larger scale-up systems.

Once the algal growth system design is fitted with the optimized custom HFM, it is the ultimate goal of the project to use flue gas from industrial plants as the feed gas to the HFM instead of pure carbon dioxide gas. A byproduct of this project in the future is harnessing plant emissions high in carbon dioxide gas; this will keep harmful greenhouse gases out of the atmosphere and will utilize the positive uses of the carbon dioxide as a food source for algal biomass for fuel production. Further exploration and expansion upon this byproduct is possible by quantitatively measuring how significant the removal of carbon dioxide gas from flue gas can be using HFM carbonation.

Experimentally determining different HFM spinning techniques that will enhance the mechanical integrity of HFM for the use in producing large quantities of algal biomass for conversion to biofuel is the ultimate goal of this project. Upon successful completion of this HFM project, the procedure for growing algae for biofuel biomass will be substantially improved and production of biofuel from algae will become more feasible in the nearer future than is currently foreseen.

REFERENCES

1. Pokoo-Aikins, Grace, Nadim, Ahmed, El-Halwagi, Mahmoud, Mahalec, Vladimir, "Design and analysis of biodiesel production from algae grown through carbon sequestration." *Clean Technical Environmental Policy,* (2010), 12:239-254.
2. Clarens, Andres, F., Resurreccion, Eleazer P, White, Mark A., Colosi, Lisa M. "Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environmental Science Technology*, (2010), 44: 1813-1819.
3. "Benefits of Oil from the OriginOil System." Retrieved January 24, 2010, from the OriginOil website: http://www.originoil.com/applications/originoil-benefits.html
4. "Algae Biofuels." Retrieved January 24, 2010, from the ExxonMobil website: http://www.exxonmobil.com/Corporate/energy_climate_con_vehicle_algae.aspx
5. Riesing, T. F. "Cultivating Algae for Liquid Fuel Production." Retrieved January 25, 2010, from Permaculture Activist Web site: http://oakhavenpc.org/cultivating_algae.htm
6. Yee, F. C. (2008). "Hollow Fiber Membranes." Retrieved January 24, 2010, from Chemical Engineering Tools and Information Web site: http://www.cheresources.com/hmembranes.shtml
7. Senthil Chinnasamy, Balasubramanian Ramakrishnan, Ashish Bhatnagar, and Keshav C. Da. "Biomass Production Potential of a Wastewater Agla *Chlorella vulgaris* ARC 1 under Elevated Levels of CO2 and Temperature" *International Journal of Molecular Sciences* (2009).

8. Carvalho, Ana P. and F. Xavier Malcata. "Transfer of Carbon Dioxide within Cultures of Microalgae: Plain Bubbling versus Hollow-Fiber Modules" *Biotechnol. Prog.* (2001), 17, 265-272.

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